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NOVEL METHOD FOR GAS PHASE CALIBRATIONS

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PREFACE

Technical Notes are published by the U.S. Army Edgewood Chemical Biological Center (ECBC) as a quick method to disseminate information to a limited audience. The information may be superseded or appear later in an ECBC technical report or special publication. The work described in this report was started in July 2005 and completed in September 2006.

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NOVEL METHOD FOR GAS PHASE CALIBRATIONS

1. INTRODUCTION

Manual calibration of analytical instruments with toxic gases is problematic, due to the numerous errors introduced by the use of uncertain equipment such as syringes, but also because of safety concerns arising from the necessary proximity of the operator to the gases and instrument. To eliminate these issues, a new, automated method and system for calibrating was developed, removing the operator from "hands-on" calibration. The system uses a stainless steel ballast tank, a series of Valco® valves, and calibrated sample loops to precisely calibrate analytical equipment with gas phase chemicals. In addition, a Labview® data acquisition program was written, which allows automatic operation of the calibration system with interface to several common laboratory analytical devices.

2. BACKGROUND

The historic method for gas phase calibration of analytical instrumentation is to use a gas-tight syringe to withdraw sample from a gas cylinder, and then inject the contents into a calibrated gas ballast for dilution. Multiple injections and dilutions may be necessary to achieve a range of calibration concentrations. Dilution of the calibration gas is followed by repetitive syringe injections of the gas mixture into a gas analyzer/detector. This method of calibration has always been problematic. Pressure differences between the pressurized gas cylinder and the syringes can cause concentrations to be higher than ideal values. Leaks have been an issue from the standpoint of analytical precision, and more so, safety. Leaks may occur from several points during the retrieval of the standard gas and delivery to the ballast, and can cause the calibration to be lower than the ideal value. Furthermore, if a leak is consistent, then the error will be systematic and an operator would not find the problem by evaluating the quality of the calibration fit. As well as impacting data quality, leaks can be a safety concern. In many cases, the analytical instrument may not be located in a hood, but is instead on the lab bench. Thus, if a syringe is leaking and the operator withdraws the syringe from the hood to inject into an analytical device, the operator is at a high risk of chemical exposure.

In addition to error from leaks, the use of a gas-tight syringe allows transfer of heat from the operator's hands to the syringe. The smaller the syringe, the more significant this heat transfer becomes. With excess heat transfer, the volume injected is less concentrated than an ideal volume. Improper syringe filling can also cause errors in calibration. Because gases are mostly colorless, it is almost impossible to determine when a syringe contains the desired volume. Differences in the time allowed for the sample withdrawal can cause differences in the volumes collected and thus injected.

3. TEST SYSTEM

It was the goal of this effort to determine a method of gas calibration for gas chromatographs (GC) and other analytical equipment. This minimizes the potential for human error and also protects the worker from potential exposure to harmful chemicals.

Rotary valves have been used for many years to deliver quantitative amounts of gases for direct injection into an analytical device. Combining the use of electrically actuated valves with stainless steel gas ballasts dramatically improved the precision, accuracy, and safety during gas calibration procedure as compared to that performed via syringe.

The new calibration system is, in principle, the same as the syringe method of gas calibration. However, instead of using a syringe to inject a known quantity of chemical into a calibrated ballast volume, a Valco® valve and calibrated gas loop are used for consistent injections. The system was constructed using two small rotary vane pumps, two electrically actuated Valco® 6 port valves with 2 calibrated 1/16" stainless steel gas loops, two 4 way valves, two 6 L stainless steel ballasts, two 4 L/min rotometers, an on/off valve, and miscellaneous tubing and fittings, as shown in Figure 1.

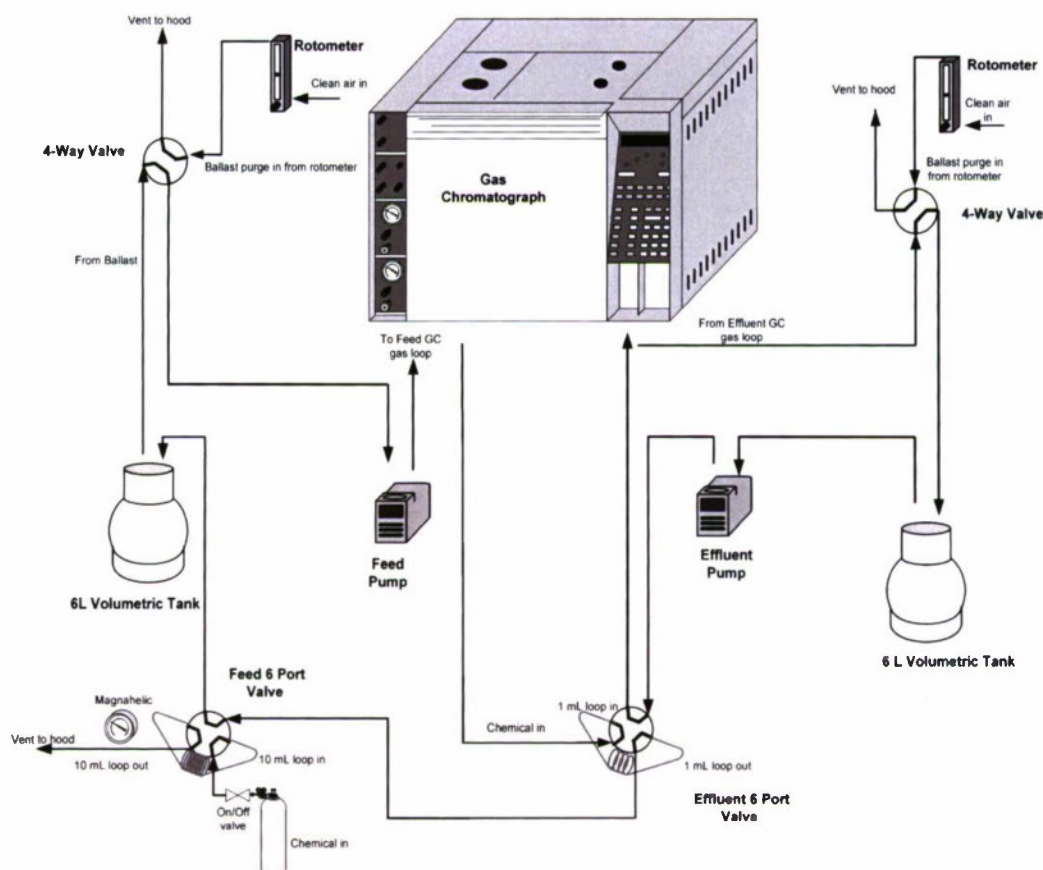


Figure 1. Ballast Calibrator System

The ballast calibration system is set up such that a 4-way valve is connected to one port of the 6 L ballast. The 4-way valve is connected on the other three sides to a rotometer regulated source of clean purge air, a vent line, and to the GC (see Figure 2). In one position, the 4-way valve allows the system to be purged with air and vented. The other position is a closed loop system connected to the GC, a rotary vane pump, 6 port rotary valve with gas sampling loops, and ballast tank.

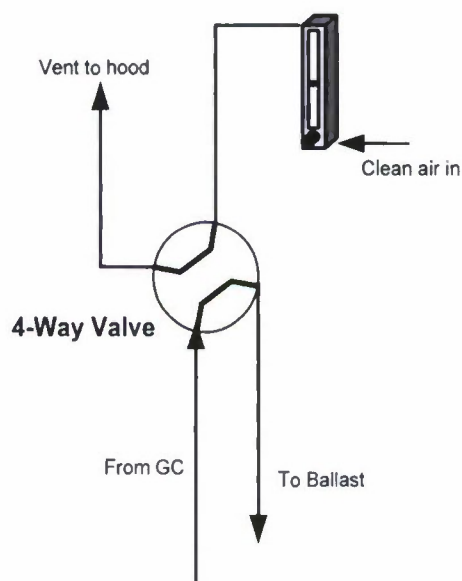


Figure 2. 4-Way Valve Connections

To introduce calibration gas sample to the ballast calibration system, a regulated source of the chemical of interest is connected to one port of the 6 port rotary valve. An appropriately sized gas loop is connected to two corresponding ports on the valve. As seen in Figure 3, the fourth connection is to a vent. The remaining connections are to and from the calibration system.

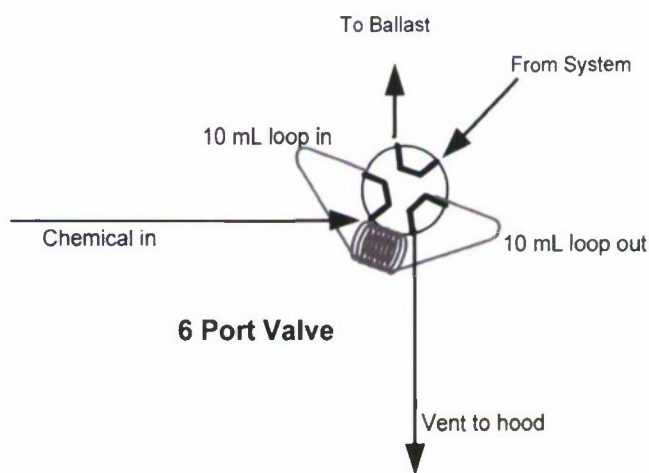


Figure 3. 6 Port Valve Connections

The 6 port Valco® valve has two positions, “load” and “inject”. In the “load”

position of the valve, the calibration chemical is allowed to flow from the source through the sample loop and out the filtered vent line. When a sufficient time has elapsed to ensure the loop is filled with calibration chemical, the source of chemical is stopped momentarily with the on/off valve to allow the loop of the calibrator system to come to atmospheric pressure as measured with a small pressure meter. The rotary valve is then changed to the “inject” position. The chemical in the loop is thus transferred to the 6 L gas ballast.

The rotary vane pump is switched on, and the contents of the ballast are mixed to ensure homogeneity. The GC, equipped with gas loop injection, is then cycled to determine a calibration curve point. Repetition of the “load” and “inject” process builds the increasing concentration required for a calibration curve.

The calibrator system has been designed to allow simultaneous calibration of a high concentration (feed) detector and low concentration (effluent) detector. This is arranged by interconnecting a second ballast in series with the first ballast. The concentration of the serial dilution is limited by the size of the second ballast, the volume of the gas loop available, and the minimum detectable limit of the detector as shown in the equation. Calibration concentrations are determined as follows:

$$C_1V_1=C_2V_2$$

where

C_1 = Concentration of incoming chemical (mg/m³)

V_1 = Volume of gas loop being used (mL)

C_2 = Calculated concentration (mg/m³)

V_2 = Pre-calculated volume of ballast (mL)

For the high level calibration, chemical is added directly from the chemical source (i.e., gas cylinder). For the low level calibration, the chemical source is the high level system. By interconnecting the systems, it allows appropriate dilutions for calibration of two detectors without any human intervention. Figure 1 details this plumbing arrangement. National Instruments Labview® program has been used to automate a calibration system such that human intervention is necessary only for the hook-up of the ballast calibrator to the calibration chemical and detector. Labview®’s timed events functions allow automatic valve switching, GC operation, and data collection.

Three potential problems may exist with this type of calibration system. Leaks can be an issue when considering the large number of fittings and connections. If at any time a leak is suspected, the calibration system is attached to a helium source in place of the purge air and can be evaluated with an electronic leak detector or magnahelic gauge. The second problem is the potential for reaction of the gas. Chemical reactions could occur either with the ballast material or with moisture that may exist inside the ballast. The ballasts are purged well with dry air (<5% H₂O) or nitrogen before any calibration takes place to ensure a moisture free environment. Control charts are kept of the calibration data to determine if the detector signal is dropping over time. Third, as it exists in this laboratory, the calibrator unit and the GC are too large to be placed inside a hood under engineering controls. Modifications certainly could be made to reduce the size of the unit. The most significant opportunity for size reduction would be

the ballast tanks. Dependant upon the calibration concentration required, the size and volume ballast tanks and sample loops could be increased or reduced per eq 1. However, the smaller the calibration system, the more significant the volume of the system tubing becomes. In addition, the system should not become so small that it becomes pressurized. The system should remain at approximately atmospheric pressure.

4. DATA/RESULTS

The calibrator system has been used to successfully calibrate gas chromatographs with FID, ECD, FPD, and TCD detectors using various toxic gases such as phosgene, hydrogen cyanide, cyanogen chloride, and ethylene oxide. In addition, it has been used to successfully calibrate Miran® infrared spectrometers and Fourier transfer infrared spectrometers with similar gas phase chemicals. For example, Figure 4 shows phosgene data collected over a 3 month period with a TCD/ECD GC. These data represent individual calibration events, generally on a weekly basis. The area counts correlate to a concentration of 20,000 mg/m³ for the high concentration analyzed by a GC-TCD and 8 mg/m³ for the low concentration detected with a GC-ECD.

The coefficient of variation of the area count values is <1.7% for the feed data and is 2% or less for the effluent. Figure 5 is a calibration curve of similar data. The points represent the four individual data points at each concentration. The correlation coefficient through zero is at least 0.998.

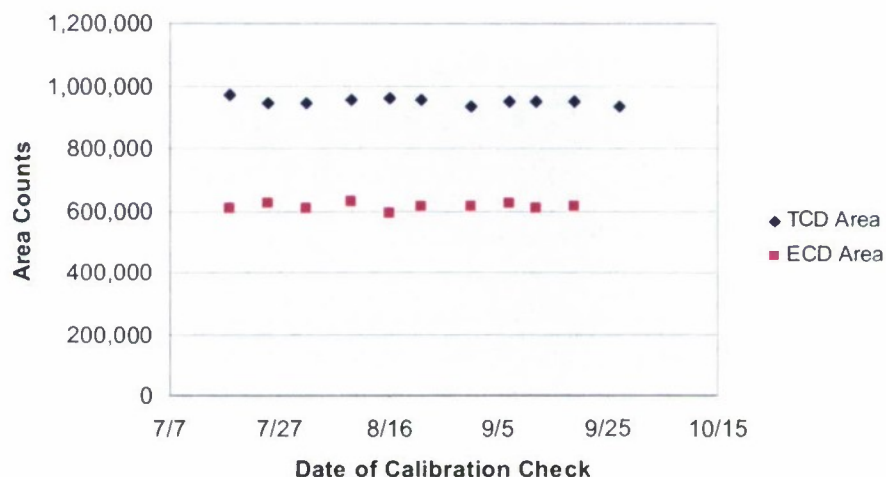


Figure 4. Control Chart of Repetitive Data Generated by the Ballast Calibrator

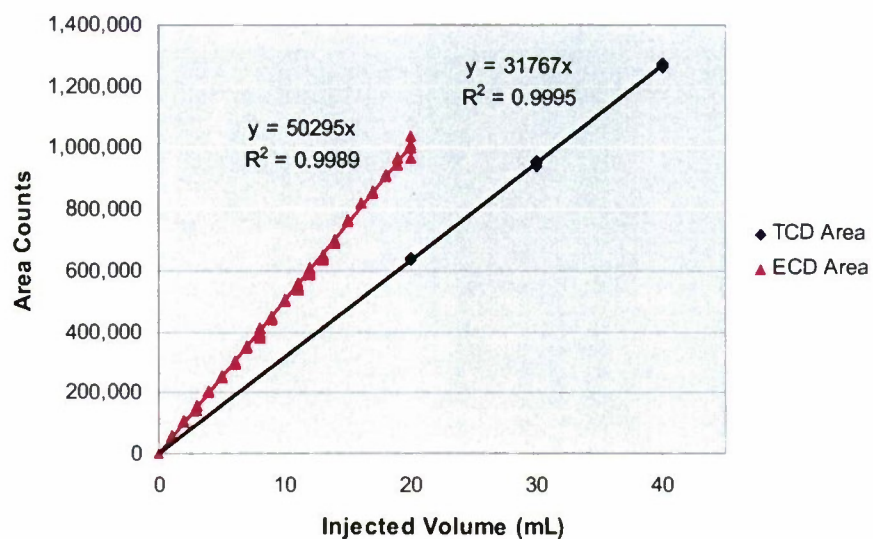


Figure 5. Phosgene Calibration from a GC -TCD /ECD

5. SUMMARY/CONCLUSION

The ease of use of this calibration system and the excellent reproducibility make it a very useful device for gas phase calibrations on several analytical detectors. The benefit of this newly developed system is that it removes the operator from the systematic part of the process when performing a calibration. Consequently, the need for syringe injections is removed, and the potential for chemical exposure is reduced. The use of gas loops increases the reproducibility of the injection volumes, thus creating a more controlled manner of sample delivery to the monitoring equipment. This unit is a safe and convenient method for calibrations with gas phase samples.